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Hot-Pressing Mixed Carbides of Ta, Hf, and Zr

JOHN J. FISCHER

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio

The effect of hot-pressing parameters (temperature, pressure, and time) on the density and grain size of two mixed carbides, 80% TaC 20% HfC and 80% TaC 20% ZrC (at.%), was investigated. The purpose of this investigation was to determine what conditions would be necessary to produce high-density bodies and what resultant grain size might be expected for a given set of conditions. The hot-pressing was accomplished by means of an inductively heated graphite die body with pressure being supplied by a hydraulic press.

Based on the computed theoretical densities used in this investigation, 4TaC·1HfC was hot-pressed to approximately 100% relative density at 4600°F and 6000 psi in 15 minutes. The maximum density achieved in the 4TaC·1ZrC composition was 96% relative density under the same conditions.

Based on grain size measurements there is evidence of a recrystallization temperature for both materials at about 4600°F under a hot-pressing pressure of 3700 psi.

The compositions 4TaC·1HfC and 4TaC·1ZrC have the highest known melting points of any materials, 7128° and 7110°F, respectively.[1] TaC forms a complete solid solution, of the NaCl structure, with HfC and ZrC.[2,3] The 80/20 at.% ratio of TaC to HfC or ZrC results in a single phase material with a melting point higher than the individual constituents. Recently the melting point maxima have been confirmed,[4,5] although the actual melting temperature varied in each case.

This investigation was undertaken to determine the effects of the hot-pressing variables, temperature, pressure, and time on the density and grain size of the two compositions. The materials were compacted by hot-pressing in graphite dies. The temperature of pressing was varied from 3450° to 4800°F, the pressure from 1000 to 7000 psi and the time from 1 to 60 minutes.

The hot-pressed pieces were in the shape of cylindrical disks, $^5/_8$ in. in diameter by approximately $^1/_4$ in. thick.

Test Material

The average particle size of the two powders* were 1.5 μ (4TaC·1HfC) and 2.8 μ (4TaC·1ZrC) as determined from Fisher Sub-Sieve Sizer measurements. Chemical analysis is given in Table I. X-ray diffraction of the as-received powders gave the following lattice parameters using CuK_α radiation and a scan speed of $^1/_4$° per minute.

$$4TaC\cdot1HfC \quad a_0 = 4.483 \pm 0.002 \text{ A}$$

$$4TaC\cdot1ZrC \quad a_0 = 4.493 \pm 0.002 \text{ A}$$

From these measurements theoretical densities for the two powders were determined. In calculating the density, Ta, Hf, Zr, and the impurity atoms were assumed to take metal atom positions in the face-centered cubic lattice. The nonmetal atoms were assumed to take carbon sites. Using the chemical analysis under the above assumptions, the weight of a unit cell was determined. The weight of a unit cell divided by the volume of the cell, as determined from X-ray measurements, gave the calculated densities. For comparison purposes, the density of the loose powder was taken by means of a Beckman Air Comparison Pycnometer. The values obtained by the two methods are in close agreement and are given below:

Pycnometer densities, g/cm³	Calculated densities, g/cm³
ρ4TaC·1HfC = 13.82 ±0.03	ρ4TaC·1HfC = 13.89
ρ4TaC·1ZrC = 12.71 ±0.03	ρ4TaC·1ZrC = 12.68

[1] C. Agte and H. Alterthum, "Untersuchungen über Systeme hochschmelzender Karbid nebst Beitragen zum Problem der Kohlenstoffschmelzung" (Researches on Systems with Carbides of High Melting Point and Contributions to the Problem of the Fusion of Carbon), *Z. tech. Physik*, **11**, 182–91 (1930); *Ceram. Abstr.*, **11** [8] 457 (1932).

[2] H. Nowotny, F. Benesovsky, and R. Kieffer, "Das hafnium-karbid und sein verhalten gegenuber anderen karbiden der hochschmelzenden ubergangsmetalle" (Hafnium Carbide and Its Behavior to Other Carbides of the High-Melting Transition Metals), *Planseeber. Pulvermet.*, **7** [2] 79–87 (1959).

[3] J. T. Norton and A. L. Mowry, "Solubility Relationships of the Refractory Monocarbides," *Am. Inst. Mining Met. Engrs. Tech. Pub.*, No. 2527; *J. Metals*, **1** [2, Sect. 3] 133–36 (1949); *Ceram. Abstr.*, **1949**, June, p. 155*g*.

[4] J. L. Engelke, F. A. Halden, and E. P. Farley, "Synthesis of New High Temperature Materials," *PB Rept.* **161720**, 44 pp.; *U. S. Govt. Research Repts.*, **34** [2] 178 (1960); *Ceram. Abstr.*, **1962**, April, p. 91*f*.

[5] P. T. B. Shaffer and R. L. Watts, "Development of Ultra Refractory Materials," Summary Rept., Nov. 1, 1960–Oct. 31, 1961, Carborundum Co., Research and Development Division, Niagara Falls, N. Y., NP-11160, Contract NOrd-17175, November 30, 1961. 48 pp.

* Supplied by the Firth Sterling Corp., Pittsburgh, Pa.

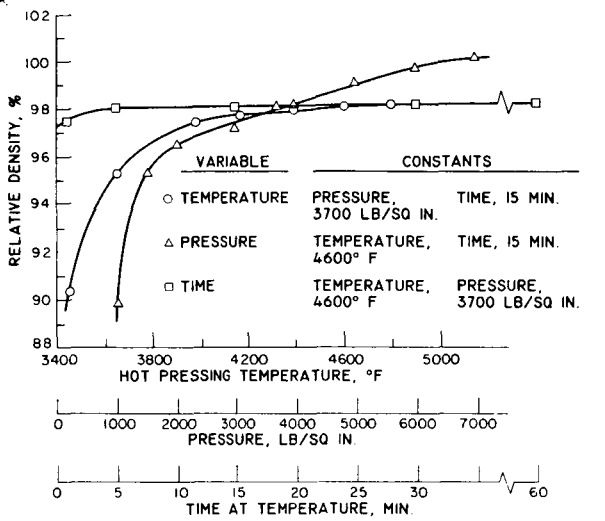

Fig. 1. Variation of relative density of 4TaC·1HfC with hot-pressing parameters

Apparatus and Procedure

The approximate range for the individual parameters, temperature, pressure, and time was established from a prior knowledge of the hot pressing parameters of HfC.[6] While investigating the effect of one parameter, the other two were held constant. The constant values were: temperature, 4600°F; pressure, 3700 psi; and time, 15 minutes.

The hot pressing dies, plungers, etc. were machined from graphite.† The assembly was heated by means of a water cooled, $7^1/_2$ in. diameter, induction coil. The coil was powdered by a 50 kw, 9600 cps motor generator.

Temperature measurements were made with an optical pyrometer that had been calibrated against a National Bureau of Standards, certified standard lamp. Temperature measurements were made on the die wall body approximately $^1/_2$ in. from the powder charge. Transmission correction of the quartz prism was also made with an N.B.S. standard lamp. Temperature readings are believed to be accurate to ±40°F.

The powder charge for each run was 12 g. The desired pressure was applied throughout the heating period and time measurements were begun when the desired temperature was reached. The values given in Fig. 2 are the actual length of time the specimen was at the specified temperature. The time necessary to reach 4600°F, for example, was 23 minutes. The average rate of cooling from 4600° to 2000°F was 100°F per minute.

At the end of the desired pressing time, the pressure was removed. Previous experience had given some indication that pieces were often cracked when the load was kept on during the cooling cycle.

Densities of the pellets were measured by the water displacement method. The relative densities given are the ratio of the measured density to the theoretical calculated density. All disks were sectioned by electric discharge machining and then examined metallographically. After polishing and etching, the disks were photographed for grain size measurements.

Both compositions were etched with a solution of 3 parts aqua regia and 1 part HF. It was further necessary to heat tint the 4TaC·1HfC composition.

The grain size measurements were made by counting the number of grains intersecting a line of known length. Each grain diameter is the average of several measurements.

Results and Discussion

Figure 1 is a plot of relative density (% RD) against the three parameters, temperature, pressure, and time for the 4TaC·1HfC composition. It can be seen in the temperature and time curves that a maximum relative density of about 98% RD is attained under the range of conditions examined. The time curve shows very little increase in density from 1 minute at temperature up to 1 hour at temperature. This indicates that much of the consolidation occurs during the time necessary to reach temperature.

The pressure curve shows a large increase in relative density over the pressure range investigated. The maximum density obtained was 100.13% RD, indicating some error in the calculated density; examination of this piece under the microscope did reveal a slight amount of porosity. The strength of the graphite die parts limited the maximum pressure to 7000 psi at 4600°F.

Figure 2 is a plot of % RD against hot-pressing temperature and pressure for the 4TaC·1ZrC composition. Both curves reach a maximum relative density of about 96%. The variation in % RD with time was not investigated for the 4TaC·1ZrC composition because of the small change en-

[6] W. A. Sanders and S. J. Grisaffe, "The Hot-Pressing of Hafnium Carbide (Melting Point, 7030°F)," *NASA (Natl. Aeronaut. Space Admin.) Tech. Note*, **D-303**, 15 pp. (1960); *Ceram. Abstr.*, **1961**, September, p. 213*a*.

† Grade CS, supplied by National Carbon Co., Division of Union Carbide Corp., New York, N. Y.

Table I. Chemical Analysis

Element		Wt%	
4TaC·1HfC	C	combined	5.82
	C	free	0.03
	Fe		0.036
	Nb		0.30
	Ti		0.13
	Ta		74.23
	Hf		18.92
	Zr		0.16
	O_2		0.18
	N_2		0.021
	H_2		0.012
4TaC·1ZrC	C	combined	6.58
	C	free	0.034
	Fe		0.042
	Si		<0.001
	Nb		0.60
	Ti		0.03
	Ta		81.27
	Hf		0.6
	Zr		10.95
	O_2		0.047
	N_2		0.0094
	H_2		0.01
	B		<0.001

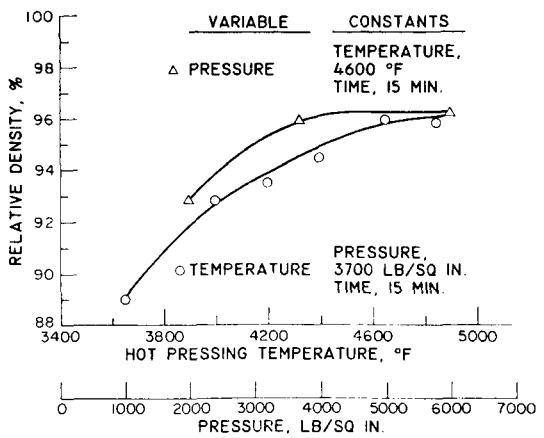

Fig. 2. Variation of relative density of 4TaC·1ZrC with hot-pressing parameters.

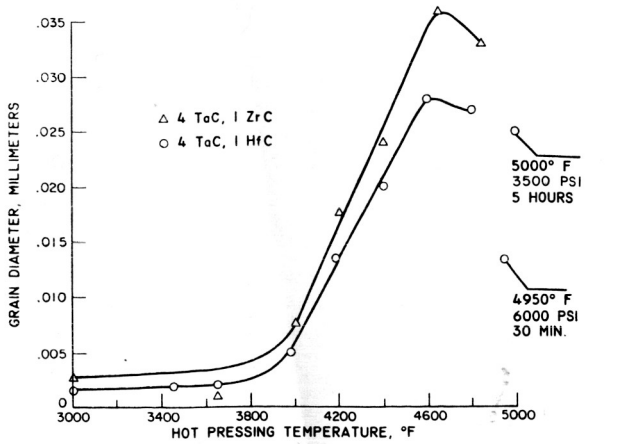

Fig. 3. Grain diameter vs. temperature at pressure of 3700 psi and pressing time of 15 minutes.

countered with the 4TaC·1HfC composition. The fact that the 4TaC·1ZrC composition could not be pressed to as high a density as 4TaC·1HfC may be due in part to the larger particle size of the starting material, 2.8μ (4TaC·1ZrC) and 1.5μ (4TaC·1HfC).

A plot of grain diameter against pressing temperature for both compositions is shown in Fig. 3. The 4TaC·1ZrC reached a maximum grain size of 0.036 mm by pressing at 4650°F. The 4TaC·1HfC had a maximum grain size, at approximately the same pressing temperature (4600°F), of 0.028 mm. The larger grain size attained in 4TaC·1ZrC may also account for its lower density. The porosity within a grain would be more difficult to remove due to the larger grain diameter. In the 4TaC·1HfC composition the grain size of pieces pressed for longer times than 15 minutes was measured. There was no increase in grain size for pressing times up to 1 hour.

The grain size of both materials was smaller at pressing temperatures greater than 4650°F. This smaller grain size may be due to the onset of recrystallization. In order to accentuate this possibility, two additional runs were made of the 4TaC·1HfC composition. A disk was pressed at 3500 psi and 5000°F for 5 hours; the resulting grain size was 0.025 mm. A second disk pressed at 6000 psi and 4950°F for 30 minutes had a grain size of only 0.0135 mm. The small grain size of this second piece, pressed at 6000 psi, indicates that recrystallization is enhanced by higher pressing loads, as would be expected. The grain diameters of these two runs are plotted in Fig. 4 for comparison purposes. Figure 4(*A*) shows the grain size of a piece pressed at 4600°F. Figure 4(*B*) shows the grain size of a piece pressed at 4950°F.

X-ray diffraction patterns were examined for relative line widths. No change in line widths was found, although a change might be expected if recrystallization were occurring due to the relief of strains. Precision X-ray diffraction patterns to specifically determine line widths were not taken.

Thus, grain size measurements suggest recrystallization; however, X-ray line width measurements do not lend support to this. If recrystallization is occurring, it could significantly alter the strength characteristics of these hot-pressed materials. In such materials high strength is obtained by high

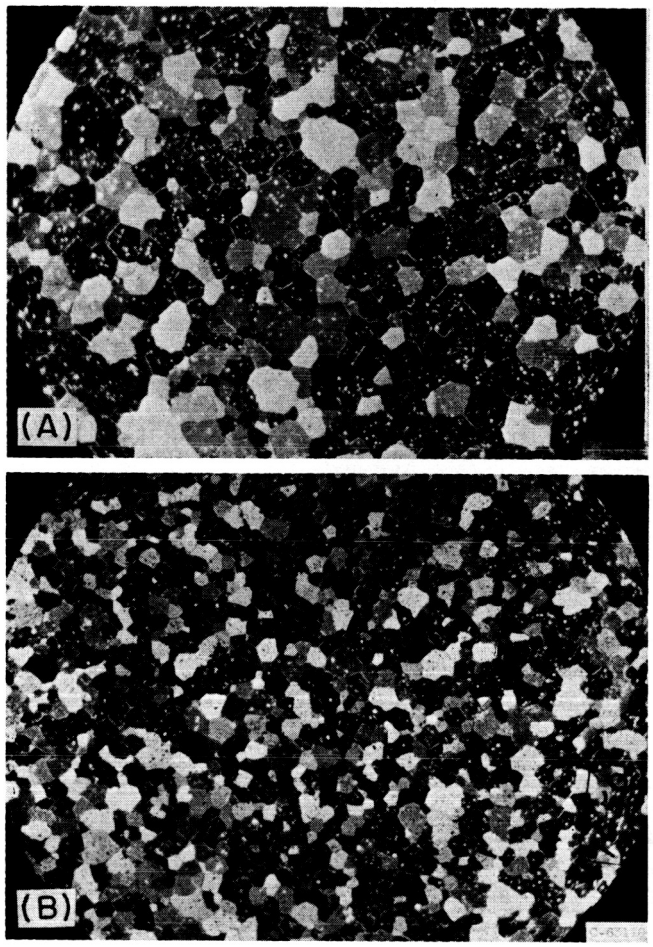

Fig. 4. Photomicrograph of 4TaC·1HfC composition. (A) Hot-pressed at 4600°F and 3700 psi for 15 minutes, grain diameter is 0.028 mm; (B) hot-pressed at 4950°F and 6000 psi for 30 minutes, grain diameter is 0.0135 mm. (Etch of 3 aqua regia—1 HF followed by heat tint; polarized light; X125.)

densities. However, the pressing temperature used to give high density results in large grain sizes which are believed to be detrimental to strength, at least in the room temperature range.* If recrystallization occurs, it presents the possibility of obtaining high density with small grain size; a combination which should give improved strength.

Microhardness measurements were made on numerous disks of each material. The average for 4TaC·1HfC was 2400 ± 100 dph (diamond-pyramid hardness). The average for 4TaC·1ZrC was 2200 ± 100 dph. A 100 g load was used in both cases. There was no noticeable change in microhardness with hot-pressing temperature or pressure.

Conclusions

The effect of hot-pressing temperature, pressure and time on the resulting density of 4TaC·1HfC and 4TaC·1ZrC was determined. The 4TaC·1HfC composition was hot-pressed to approximately 100% RD by pressing at 4600°F and 7000 psi for 15 minutes. Ninety-six percent RD was realized in the 4TaC·1ZrC composition by pressing at 4600°F and 6000 psi for 15 minutes.

For both materials, it was found that the grain size increased with hot-pressing temperature up to about 4600°F. The grain size on pieces pressed above this temperature was lower, indicating the possibility of recrystallization occurring at or about 4700°F. ☆

* The effect of grain size on strength may, of course, vary with temperature; however, this variation is not known for these materials.